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CITATION:

Suga, T ...[et al]. Characterization of nanotextured AlN thin films by x-ray absorption near-edge structures. APPLIED PHYSICS LETTERS 2005, 86(16): 163113.

ISSUE DATE:

2005-04-18

URL:

<http://hdl.handle.net/2433/39671>

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# Characterization of nanotextured AlN thin films by x-ray absorption near-edge structures

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(Received 29 November 2004; accepted 2 March 2005; published online 15 April 2005)

AlN thin films have been grown on *c*-cut sapphire substrates by pulsed-laser deposition. The film epitaxially grown at 1073 K under vacuum of  $5 \times 10^{-4}$  Pa was used to examine the crystallographic orientation dependence of Al *K*-edge x-ray absorption near-edge structures (XANES), which satisfactorily agrees with theoretical spectra obtained by first-principles calculations. The film grown at 1073 K with N<sub>2</sub> backfill of  $7 \times 10^{-2}$  Pa shows nanotextured structure with its *c* plane parallel to the substrate. Although the nanotexture is not evident by x-ray diffraction, XANES can unambiguously indicate the texturing. Cross-sectional high-resolution electron microscopy provides the evidence of the nanostructure. © 2005 American Institute of Physics. [DOI: 10.1063/1.1904714]

III-V nitrides based light emitting devices have been massively used in modern technology. They are commercially fabricated mainly by metalorganic chemical vapor deposition (MOCVD) technique. Pulsed-laser deposition (PLD) is an emerging technique, which has some advantages compared to other techniques. Basically PLD can avoid impurity to incorporate into the film. Microstructure and stoichiometry of the film can be controlled by deposition parameters such as substrate temperature, deposition rate, atmosphere, laser power, etc.

PLD of AlN has been reported by a number of researchers.<sup>1–7</sup> A *c*-cut sapphire is often used as a substrate. When a *c*-cut sapphire is used, AlN is known to grow toward the *c* direction. Quality of the crystalline thin film increases as increment of the substrate temperature.<sup>5,7</sup> Although results by different groups somehow scatter, low nitrogen backfill pressure of approximately  $10^{-3}$  Pa and substrate temperatures above 1000 K with KrF\* laser have been a typical condition for the film growth of good quality.

Such films are primarily characterized by x-ray diffraction (XRD). When samples are found to show good crystallographic quality, other techniques including Rutherford backscattering, ion channeling spectroscopy, cross-sectional transmission electron microscopy (XTEM), etc., are employed for further characterization. In order to study the growth mechanism of the film, however, detailed characterization of films with poor crystallographic quality is mandatory.

In the present study, we report a technique to quantitatively characterize nanotexture of the film using x-ray absorption near-edge structure (XANES) technique. The method is extremely useful when the crystallite size is too small or too much faulted/strained to be analyzed by conventional XRD technique.

XANES has been recognized as a powerful tool to investigate electronic structures and chemical bondings around objective atoms in materials. Samples need not be crystals.

Either amorphous or liquid samples can also be characterized. Using synchrotron radiation facilities, one can obtain experimental XANES from an ultrathin film with thickness of nano to subnanometer. However, the application of XANES has been limited because of lack of a standard method to interpret an experimental spectrum. Recently, first-principles calculations using a large supercell with a core hole have been systematically made by the group of the present authors.<sup>8–13</sup> They have succeeded in reproducing and interpreting XANES of many different kinds of compounds. In this study, we use the same method to analyze the nanotexture of the AlN thin film obtained by PLD.

The thin films were made by PLD using a KrF\* excimer laser ( $\lambda = 248$  nm,  $\tau = 25$  ns, Lambda Physik COMPex205) with pulse rate of 5 Hz. Substrates were *c*-cut sapphire. Sintered AlN compact was used as a target. The distance between the target and substrate was 70 mm. Residual pressure of the vacuum chamber was  $5 \times 10^{-4}$  Pa. Many samples were made under these conditions. Among them, we have supplied three different samples for XANES. Sample A was deposited with laser power of 600 mJ ( $9 \text{ J/cm}^2$ ) without N<sub>2</sub> gas backfill. Sample B was deposited with laser power of 340 mJ ( $5 \text{ J/cm}^2$ ) with N<sub>2</sub> pressure of  $7 \times 10^{-2}$  Pa. Substrates were heated at 1073 K for samples A and B. Sample C was made under an identical condition as sample A except for the fact that the substrate temperature was 373 K. Thickness of these films was approximately 200 nm.

Crystalline quality and texture of the deposited films were investigated by XRD (Rigaku, RINT 2000) using Cu *K* $\alpha$  radiation. Figures 1(a), 1(b), and 1(c) shows x-ray diffraction patterns of three samples. Sample A shows only one reflection peak which corresponds to the (0 0 0 2) reflection of wurzite-AlN (w-AlN) crystal. On the other hand, samples B and C do not show clear reflection peaks in any  $2\theta$  range except for those from sapphire substrates. Sample B exhibits a tiny and broad reflection in the  $2\theta$  range between 30 and 38° that cannot be identified clearly. No peaks due to face-centered cubic metallic Al were observed in these samples.

Pole figure was obtained by rotating the sample around the axis that was normal to its surface ( $\phi$  scan) and around the axis that was formed by the intersection of the sample

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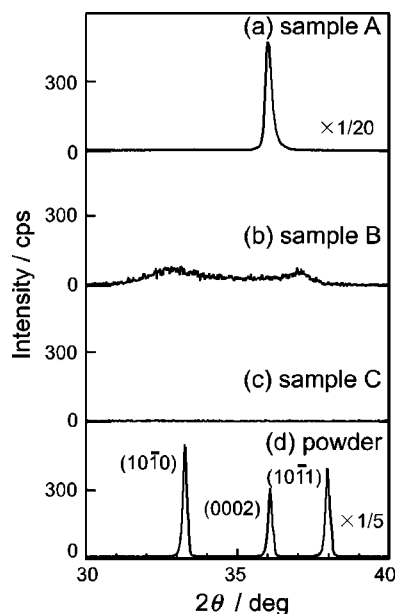


FIG. 1. X-ray diffraction (Cu  $K\alpha$ ) of four samples: (a) sample A grown at 1073 K under  $5 \times 10^{-4}$  Pa, (b) sample B grown at 1073 K under  $N_2$  of  $7 \times 10^{-2}$  Pa, (c) sample C grown at 373 K under  $5 \times 10^{-4}$  Pa and (d) w-AlN powder.

surface and the plane defined by the x-ray beam and detector ( $\chi$  scan). Sample A shows a clear sixfold symmetry of the AlN(1 0  $\bar{1}$  1) reflections indicating that the AlN film is epitaxially grown on the substrate with the relationship of AlN(1 0  $\bar{1}$  0)//Al<sub>2</sub>O<sub>3</sub>(1 1  $\bar{2}$  0). The in-plane relationship shows a 30° rotation of the AlN thin film with respect to the Al<sub>2</sub>O<sub>3</sub> substrate in the *ab* plane. They are identical with previously reported results of PLD and MOCVD-AlN film on *c*-cut sapphire.<sup>14,15</sup>

XANES were obtained at two synchrotron facilities, i.e., ALS BL6.3.1 and KEK-PF BL-11A, by total electron yield method with 2400 and 1200 line/mm grating monochromators, respectively. All measurements of XANES spectra were carried out in vacuum at room temperature. Measurement of the thin film was made on a sample after coating it by evaporated carbon to minimize charging. Powder w-AlN mounted on adhesive carbon tapes was used as a reference sample.

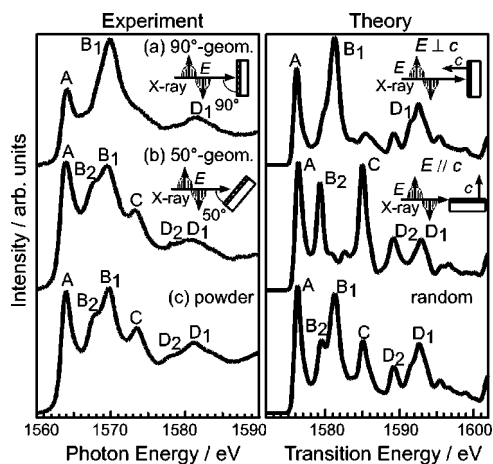


FIG. 2. (Left) Experimental XANES measured at KEK-PF: (a) sample A measured with 90° geometry, (b) sample A measured with 50° geometry, and (c) w-AlN powder. (Right) Theoretical XANES by first-principles OLCAO method with  $E//c$ ,  $E \perp c$  and random conditions.

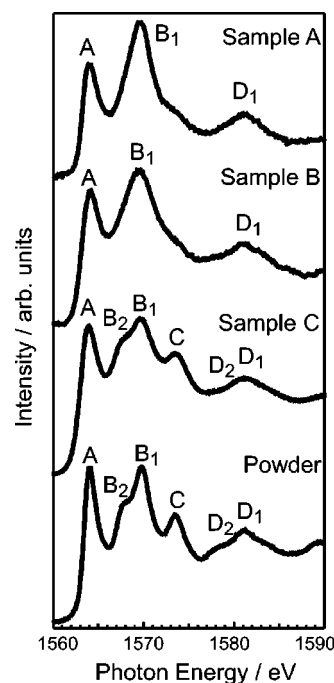


FIG. 3. Experimental XANES measured at ALS with 90° geometry.

The left panel of Fig. 2 shows experimental XANES of sample A in comparison to that of w-AlN powder measured at KEK-PF. Sample A was mounted in two different geometries with its surface 90° and 50° to the incident x-ray beam. When measured with the 50°-geometry, XANES of sample A is identical to that of w-AlN powder. The angle is close to  $\cos^{-1}(1/\sqrt{3})=54.7^\circ$ , which should provide averaged XANES of all crystallographic directions.<sup>16</sup> When measured with the 90° geometry, however, peaks B<sub>2</sub>, C, and D<sub>2</sub>, as denoted in Fig. 2(b), remarkably lost their intensity. Given the fact that the sample A exhibits a high degree of texturing along the *c* axis normal to the substrate, peaks B<sub>2</sub>, C, and D<sub>2</sub> should be ascribed to the XANES components that appears only when measured with  $E//c$  condition where  $E$  is the electric field vector and  $c$  is the *c* axis of the hexagonal crystal.

In order to confirm the interpretation, first-principles orthogonalized linear combination of atomic orbitals (OLCAO) method was employed. This is a band structure calculation based on the density functional theory within local density approximation.<sup>17</sup> In the calculation, experimentally reported crystal structure<sup>18</sup> was used. On the electron transition process associated with XANES, an electronic hole at a core orbital was generated, which is called a core hole. In the calculation, the initial state (ground state) and final state (core-holed state) were calculated separately. A core hole was included in an Al 1s orbital. Matrix elements of electric dipole transition between the initial state and final states were rigorously computed using wave functions of the two states. In order to minimize artificial interactions among core holes under periodic boundary condition, a large supercell composed of 108 atoms has been adopted. All theoretical XANES were obtained by broadening the theoretical spectra with Gaussian functions of 1.0 eV full width at half maximum. Theoretical transition energy was obtained as the total energy difference between the final and the initial states. The right panel of Fig. 2 shows theoretical XANES with  $E//c$ ,  $E \perp c$  and random conditions, which were partially shown in our previous letter.<sup>13</sup> Line shape of the theoretical

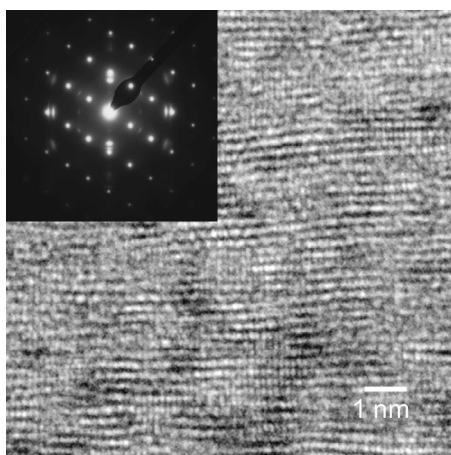


FIG. 4. XTEM of sample B. Inset shows electron diffraction pattern obtained from a large area that contains both substrate and thin film.

spectrum of w-AlN (random) satisfactorily reproduces that of the w-AlN powder. Increase in intensity of peaks  $B_2$ , C, and  $D_2$  is evident in the  $E//c$  condition, which is also in good agreement with the experimental spectra. We can therefore conclude that the absence of peaks  $B_2$ , C, and  $D_2$  can be a good fingerprint to the preferred orientation of  $c$  perpendicular to the film surface.

Experimental XANES from three samples with the  $90^\circ$  geometry measured at ALS are displayed in Fig. 3. XANES of sample A and powder sample measured with at different light source are in perfect agreement. XANES of sample C is found to be close to that of crystalline w-AlN powder. This implies that the local atomic environment and chemical bondings of AlN in sample C, which is amorphous by XRD, should be very close to that of w-AlN. They should be randomly oriented. It is very interesting to note that the XANES of sample B resembles that of sample A although texturing of crystals is not evident by XRD in sample B. Careful inspection can find that the intensity ratio of  $B_1$  and A is smaller in sample B. Peak  $B_1$  is broader in sample B. The most probable interpretation of the XANES of sample B should be the nanosized texturing of AlN crystallites along the  $c$  axis perpendicular to the substrate. Smaller relative intensity of peak  $B_1$  would suggest that the texture is not perfect in sample B as in sample A.

To confirm the hypothesis, XTEM observation has been made on both samples A and B. TEM samples were made by a standard technique including dimpling and ion milling. In order to minimize the damage during the ion-milling procedure, samples were cooled using liquid  $N_2$ . Observations were made using a TEM equipped with a field emission-type electronic gun (Philips CM200FEG). Sample A is composed of a single crystal AlN film with dense threading dislocations. On the other hand, the sample B is found to be composed of a nanotextured structure as shown with a high-

resolution image shown in Fig. 4. The size of crystallites is approximately 2 nm. They are aligned so as to make  $c$  perpendicular to the substrate. Using the Scherrer equation for the broadening of the XRD peaks, 2 nm of crystallites diameter may correspond to the peak width of  $6^\circ$  at  $2\theta=36^\circ$  even in the absence of strain. The XTEM result is therefore consistent with the XRD data showing very broad reflections. The presence of a small distortion of crystallites in the nanotextured structure is also consistent to the XANES data which indicates that the alignment of crystallites is not perfect in sample B as in sample A. We can conclude that features of the nanotextured structure in the thin film are well characterized by the XANES analysis.

The authors would like to thank Dr. R. C. C. Perera and Dr. P. Nachimuthu of Lawrence Berkeley Laboratory for their assistance with XANES measurements at ALS, and Professor Wai Yim Ching for allowing the authors to use the OLCAO code. This work was supported by three projects from the Ministry of Education, Culture, Sports, Science and Technology of Japan. They are Grant-in-Aid for Scientific Research on Priority Areas (No. 751), the Computational Materials Science Project in Kyoto University, and the 21st century COE program. One of the authors, T.M., is a JSPS research fellow.

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